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ELASTOMER COMPOSITION CONTAINING AN INTERNAL RELEASE AGENT WITH URETHANE AND/OR UREA BASE

Inventor:	Klaus Steichele
Applicant:	Company known as: CARL FREUDENBERG resident in the Federal Republic of Germany
Grantee:	[Same as above]
Agent:	Cabinet Beau de Lomenie 55, rue d'Amsterdam, 75008 Paris

The present invention refers to an elastomer composition that is easy to release because of the presence of an internal release agent with urethane and/or urea base.

Elastomers are well-known products and have multiple applications, in particular for the production of molded pieces as resistant materials and elastic materials. The mixture used may be put in the desired shape by injection or recoil in a tool, and curing by heating.

To avoid the bonding of the cured molded piece on the wall of the mold, the use of a release agent is essential. The most common operating method consists of carefully applying a thin layer of release agent in the tool before the introduction of the rubber mixture. Usually, waxes, soaps or oils are used. These release agents, called "external," give good results but it is necessary to apply them in a separate operation. During this operation, the tool is absent from production. The exact measurement of the release agent is often difficult because it is applied by spraying or spreading, and in the case of molds with a complicated shape, for example, molds with fine etching, it is difficult to achieve a complete coating.

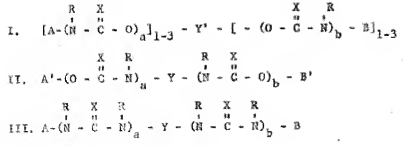
Because of the difficulties described above, "internal" release agents have been developed, for example for the production of pieces molded from polyurethane which consist of fatty acid derivatives most of the time. The fatty acid derivatives are added in a relatively high quantity to the polyurethane composition and contribute to correct release of the piece. However, in the automatic production of molded pieces, the utility of these internal release agents is limited because after several production cycles, a soiling of the mold is observed, requiring interruption of the automatic operations. In addition, the level of mechanical properties of the molded pieces is affected by the relatively high amounts of internal release agents. Such internal release agents for polyurethanes are described in the Federal Republic of Germany patent applications published under Nos. DOS 2,307,589 and 2,319,648.

The applicant has researched an appropriate release agent for use with the elastomer mixtures and enables automatic production of the molded pieces for long periods without soiling the tool and without diminishing the level of mechanical properties of the molded pieces.

Other purposes and advantages of the invention will appear from reading the description below.

These purposes and advantages have been achieved in an internal release agent which has an oligomer composition and as a characteristic, carries a group that has an affinity for the elastomer groups of the macropolymer. Such groups that have this affinity consist of urethane and/or urea groups or respectively, thiourea or thiourethane.

Therefore, the invention has as a goal an elastomer composition that is easy to release formed of a macromolecular elastomer and an internal release agent, characterized in that the internal release agent consists at least of an oligomer product with urethane, urea base, or their mixtures fulfilling one of the following formulas:



in which A, A', B, B' and R independently of each other represent C_1-C_{35} alkyl residues or residues of substituted aryl esters, the substituents of the aryl esters being halogen atoms, C_1-C_{35} alkyl residues or C_6-C_{14} aryl, C_1-C_{15} alkylthio, C_6-C_{14} arylthio or C_7-C_{15} arylalkyl residues, A, B and R also may be hydrogen atoms, but at least one of the A, B and R residues is not hydrogen, and the X residues are oxygen or sulfur atoms, the Y and Y' residues, independently of each other, being C_1-C_{35} alkylene, C_6-C_{14} arylene, C_7-C_{30} alkylarylene,

C_7-C_{20}, $-(CH_2)_{1-4}-O-(CH_2)_{1-4}$ and $-(CH_2)_{1-4}-S-(CH_2)_{1-4}$ arylalkylene, residues or residues of polyethers, polycarbonates or polybutadiene with molecular weight from 400-4000, and a and b are whole numbers on condition that the sum a + b is at least equal to 1.

The oligomer products are added to the macromolecular mixture at 0.01-10.0 parts by weight for 100 parts by weight. For most applications, a quantity of 0.1-2.0 has given the best results.

The elastomer raw materials may consist of commercial elastomers, for example, natural rubber, synthetic rubbers such as styrene-butadiene rubber, butyl rubber, polysulfide rubber, nitrile-butadiene rubber, chlorosulfonated polyethylene, silicone rubber, fluorinated rubber, ethylene/propylene rubber, EPDM rubber, ECO rubber, polynorbornene rubber, acrylate rubbers, chlorinated polyethylene, chlorobutyl rubber, bromobutyl rubber, isoprene rubber, ethylene-acrylate rubber, chloroprene rubber, ethylene-vinyl acetate rubber, polybutadiene rubber, polyether-ester elastomer, phosphorus-nitrile rubber and fluorosilicone rubber with the usual filler materials, auxiliary systems and crosslinking systems.

The oligomer products are added in small amounts to the individual components of the elastomer composition before rolling or mixing. The oligomer urethanes or ureas are prepared in a manner known in itself. These are reaction products of monofunctional isocyanates with alcohols and/or mono or polyfunctional amines or reaction products of diisocyanates with alcohols and/or mono- or polyfunctional amines. These oligomer products may also carry reactive groups with the crosslinking system.

The internal release agents according to the invention must fulfill the general formulas given above. Particularly satisfactory results have been obtained with distearylurethane.

The following will be mentioned as being among the most highly rated products, for example: the reaction products of monoisocyanates such as the monoisocyanates containing 6 to 18 carbon atoms, for example, stearyl isocyanate and/or palmitin isocyanate, if need be in the mixing state with monoalcohols. Among the monoalcohols that have given the best results, the C_6-C_{18} alcohols will be mentioned in particular, for example, stearyl alcohol or palmitic alcohol. Alcohols containing double bonds, for example, oleyl alcohol, alcohols containing epoxide groups such as glycide and epoxidized fatty alcohols are also suitable.

In numerous cases, a quantity of 0.5-1.0 part by weight, for 100 parts by weight of the elastomer mixture, already gives good results.

With the elastomer composition according to the invention, molded pieces of pure rubber are prepared as well that are easy to release, for example bellows, rings, cylinders, covers, joints, as well as metal-rubber pieces that are easy to release, for example, shock absorbers and shaft sealing rings.

The examples that follow illustrate the invention without, however, limiting the scope. In these examples, information concerning parts and percentages refer to weight, except where mentioned to the contrary.

Examples

The examples that follow describe the preparation of oligomer urethanes that act as internal release agents. The preparation methods described in the examples may be used for oligomer urethanes, ureas and thiourethanes. In these methods, the mono- or polyisocyanate and the compound containing the active hydrogen are mixed with each other and heated at high temperature, preferably at 130°C. After a reaction time of approximately 30 min, the product is poured in a cold plate where it solidifies. It is broken, and then, the reaction product may be used as is.

Table

① Agent de démoulage (M)	② Composant (OH/NH)	(NCO)	③ Point de fusion, °C
1	éthylèneglycol ⑤	stéaryl-isocyanate	99,5
2	propane-diol-1,3	"	94
3	butane-diol-1,4	"	103
4	butane-diol-2,3	"	106
5	glycol néopentylique	"	59
6	hexane-diol-1,6	"	117
7	dodécane-diol-1,12	"	102
8	diéthylène-glycol	"	93
9	thioglycol	"	81
10	hexane-diol, butane-diol, 1:1	"	98
11 ④	éther de bis(hydroxyéthyle) d'hydroquinone	"	171
12	polycaprolactonediol (PM 500)	"	73
13	polytétrahydrofurannediol (PM 650)	"	64
14	3 moles de triméthylolpropane + (1 mole d'isocyanate de stéaryle)	"	41
15	2 moles de triméthylolpropane + (1 mole d'isocyanate de stéaryle)	"	51
16	triméthylolpropane éthoxylé vendu par la Société BASF sous le nom de VP 820-OH	"	-
17	triméthylolpropane propoxylé vendu par la Société BASF sous le nom de (VP 830-OH)	"	-
18	polyéthylène-glycol PM 200	"	-

Key: 1 Release agent (M)
2 Component (OH/NH)
3 Melting point. °C

4 Ethylene glycol
1,3-Propanediol
1,4-Butanediol
2,3-Butanediol
Neopentyl glycol
1,6-Hexanediol
1,12-Dodecanediol
Diethylene glycol
Thioglycol
Hexanediol, butanediol, 1:1
Hydroquinone bis(hydroxyethyl) ether
Polycaprolactonediol (MW 500)
Polytetrahydrofurandiol (MW 650)
3 mol trimethylolpropane + (1 mol stearyl isocyanate)
2 mol trimethylolpropane + (1 mol stearyl isocyanate)
Ethoxylated trimethylolpropane sold by the BASF Company under the name VP 820-OH
Propoxylated trimethylolpropane sold by the BASF Company under the name (VP 830-OH)
Polyethylene glycol MW 200
5 Stearyl isocyanate

Table (cont'd 1)

(1) Agent de démoulage (M)	(2) Composant (OH/NH)	(NCO)	(3) Point de fusion, °C
19	polyéther à groupes silicone vendu par la Société Dow Corning sous le nom de DC 1248	stéaryl-isocyanate (5)	liquide
20	polyéther à groupes silicone vendu par la Société Dow Corning sous le nom de DC 43667	"	liquide
21	polybutadiènediol vendu par la Société Metallgesellschaft sous le nom de Poly bd CS 15	"	liquide
22	polybutadiènediol vendu par la Société Metallgesellschaft sous le nom de Poly bd R 45	"	liquide
23	2-éthylhexanol	"	63
24 (4)	butanol-1	"	68
25	hexanol-1	"	58
26	alcool stéarylique	"	75
27	méthylbutène-3-ol	"	63
28	hexyne-3-diol-2,5	"	81
29	butène-2-diol-1,4	"	92
30	butène-1-ol-3	"	80
31	2-éthylhexylamine	"	84
32	hydroxypropylstéarylamine	"	94
33	triméthylhexaméthylène-diamine	"	91
34	diaminohexane	"	177

(6)

Key: 1 Release agent (M)
2 Component (OH/NH)
3 Melting point, °C
4 Polyether with silicone groups sold by the Dow Corning Company under the name DC 1248
Polyether with silicone groups sold by the Dow Corning Company under the name DC 43667

Polybutadienediol sold by the Metallgesellschaft Company under the name Poly bd R 45
2-Ethylhexanol
1-Butanol
1-Hexanol
Stearyl alcohol
Methylbuten-3-ol
2,5-Hexyne-3-diol
1,4-Butene-2-diol
3-Buten-1-ol
2-Ethylhexylamine
Hydroxypropylstearylamine
Trimethylhexamethylenediamine
Diaminohexane

5 Stearyl isocyanate

6 Liquid

Table (cont'd 2)

(1) Agent de démoulage (M)	(2) Composant (OH/NH)	(NCO)	(3) Point de fusion, °C
35	alcool stéarylique	4,4'-diisocyanatodiphényl-méthane (MDI)	142
36	alcool stéarylique	1,6-hexaméthylènediisocyanate (HDI)	126
37	alcool stéarylique	toluylènediisocyanate (TDI)	97
38	polyéther vendu par la Société BASF sous le nom de Lupranol 1004	stéarylisocyanate	-
39	hydrazine	"	200
40	alcool oléylique	"	52
41	alcool gras vendu par la Société Henkel sous le nom de Eutsnol G	"	58
42	alcool stéarylique	prépolymère de MDI+dipropyléneglycol (D'dur PF, produit commercial de la demanderesse)	140
43	alcool stéarylique	MDI à groupes carbodiimide (D'dur CD, produit commercial de la demanderesse)	144
44	éthylènediamine	stéarylisocyanate	132
45	glycide	"	56

(4) (5) (6)

Key:
1	Release agent (M)
2	Component (OH/NH)
3	Melting point, °C
4	Stearyl alcohol
	Stearyl alcohol
	Stearyl alcohol
	Polyether sold by the BASF Company under the name Lupranol 1004
	Hydrazine
	Oleyl alcohol
	Fatty alcohol sold by the Henkel Company under the name Eutanol G
	Stearyl alcohol
	Stearyl alcohol
	Ethylenediamine
	Glycide
5	4,4'-Diisocyanatodiphenylmethane (MDI)
	1,6-Hexamethylenediisocyanate (HDI)
	Toluylenediisocyanate (TDI)
	Stearylisocyanate
6	Prepolymer of MDI + dipropylene glycol (D'dur PF, commercial product of the applicant)
	MDI with carbodiimide groups (D'dur CD, commercial product of the applicant)
	Stearylisocyanate

The elastomer mixture with the composition according to the invention and which contains an internal release agent is transformed to a test-piece plate by the usual compression molding techniques.

Example 1

Nitrile rubber (with 33% ACN)	100 parts by weight
Zinc oxide	5 "
Stearic acid	0.5 "
Carbon black	40 "
Poly-2,2,4-trimethyl-1,2-dihydroquinoline	1
Dicumyl peroxide	2

Example 2

As in Example 1 with one part by weight of the additive No. 26 from the above table.

Example 3

Ethylene-propylene ternary copolymer	100 parts by weight
Zinc oxide	5 "
Carbon black	40 "
Poly-2,2,4-trimethyl-1,2-dihydroquinoline	0.5 "
Dicumyl peroxide	3.0 "

Example 4

As in Example 3 with 1 part by weight of additive No. 26.

Example 5

Vinylidene fluoride-hexafluoropropylene copolymer with integrated crosslinking system	100 parts by weight
Magnesium oxide	3 "
Carbon black	30 "
Calcium hydroxide	6 "

Example 6

As in Example 5 with 1 part by weight of additive No. 26.

No difference is observed in the appearance of the molded pieces after 6 months of storage.

The elastomer compositions of Examples 1 to 6 are subjected to tests during which they are transformed into rings by the compression technique. The number of release cycles was determined for an assessment of the release effect. A release agent is considered as optimal when the mixture can be subjected to practically unlimited releases.

(1) Mélanges élastomère de l'exemple n°	(2) Nombre de cycles	(3) nettoyage de l'outil au bout de
1	agent de démoulage extérieur nécessaire au bout de 4 cycles	au bout de 200 cycles (5)
2	interruption à 1000 cycles	outil propre après (6) 1000 cycles
3	agent de démoulage extérieur nécessaire au bout de 4 cycles	au bout de 200 cycles (7)
(4)		
4	interruption à 1000 cycles	outil propre au bout de 1000 cycles (8)
5	agent de démoulage extérieur nécessaire au bout de 3 cycles	
6	interruption à 50 cycles	

Key:
1 Elastomer mixtures of Example No.
2 Number of cycles
3 Cleaning of the tool at the end of
4 External release agent necessary at the end of 4 cycles
Interruption at 1000 cycles
External release agent necessary at the end of 4 cycles
Interruption at 1000 cycles
External release agent necessary at the end of 3 cycles
Interruption at 50 cycles
5 At the end of 200 cycles
6 Tool clean after 1000 cycles
7 At the end of 200 cycles
8 Tool clean at the end of 1000 cycles

The release effect was checked with other elastomers.

Example 7

Natural rubber	100 parts by weight
Zinc oxide	5 "
Stearic acid	2 "
N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD)	1 "
Carbon black	50 "
Aromatic plasticizer	10 "
Sulfur	2.5 "
N-Cyclohexyl-2-benzothiazylsulfenamide (CBS)	0.8 "

Example 8

As in Example 7 but with 1 part by weight of additive No. 26.

Example 9

Polyacrylate rubber	100	parts by weight
Stearic acid	1	"
Carbon black	50	"
Sodium stearate	2.5	"
Potassium stearate	1.0	"
Sulfur	0.3	"

Example 10

As in Example 9 with 1 part by weight of additive No. 26.

Example 11

Polychloroprene rubber	100	parts by weight
Stearic acid	1	"
Magnesium oxide	4	"
Carbon black	30	"
Carbon black [sic]	30	"
Dioctyl sebacate	10	"
Agent for protecting against aging		
Phenyl-β-naphthylamine (PBN)	1	"
Agent for protecting against aging		
N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD)	1	"
Zinc oxide	5	"
Ethylenethiourea	0.8	"
Tetramethylthiuram disulfide	1.0	"

Example 12

As Example 11 but with 1 part by weight of additive No. 26.

Example 13

Styrene-butadiene rubber	100	parts by weight
Zinc oxide	5	"
Stearic acid	2	"
N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD)	1	"
Carbon black N-375	40	"
Aromatic plasticizer	10	"
Sulfur	1.8	"
N-Cyclohexyl-2-benzothiazylsulfenamide (CBS)	1.0	"
Tetramethylthiuram disulfide	0.2	"

Example 14

As Example 13 but with 1 part by weight of additive No. 26.

Molded pieces were prepared with compositions of Examples 7 to 14, and the number of possible release cycles was determined.

① Mélange élastomère de l'exemple n°	② Nombre de cycles	③ Type de la pièce moulée
7	agent de démoulage extérieur nécessaire au bout de 3 cycles	pièce de caoutchouc-métal
8	interruption au bout de 50 cycles	pièce de caoutchouc-métal
9	agent de démoulage extérieur nécessaire au bout de 4 cycles	bague d'étanchéité d'arbre
10	interruption au bout de 50 cycles	bague d'étanchéité d'arbre
11	agent de démoulage extérieur nécessaire au bout de 2 cycles	soufflet
12	interruption au bout de 50 cycles	soufflet
13	agent de démoulage extérieur nécessaire au bout de 4 cycles	pièce moulée en caoutchouc
14	interruption au bout de 50 cycles	pièce moulée en caoutchouc

④ ⑤

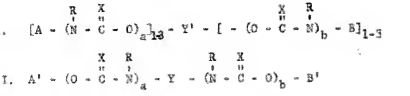
Key: 1 Elastomer mixtures of Example No.
2 Number of cycles
3 Type of piece molded

4	External release agent necessary at the end of 3cycles
	Interruption at the end of 50 cycles
	External release agent necessary at the end of 4 cycles
	Interruption at the end of 50 cycles
	External release agent necessary at the end of 2 cycles
	Interruption at the end of 50 cycles
	External release agent necessary at the end of 4 cycles
	Interruption at the end of 50 cycles
5	Rubber-metal piece
	Rubber-metal piece
	Shaft sealing ring
	Shaft sealing ring
	Bellows
	Bellows
	Molded rubber piece
	Molded rubber piece

The internal release agents are incorporated in the macromolecular elastomer composition by any means. A particularly satisfactory operating method consists of dissolving or dispersing the internal release agents in the starting compounds of the preparation of the macromolecular elastomer compositions. If one does not want it, or if it is not possible, they may be incorporated during the thermoplastic work of the elastomer composition during the plasticization operation. In numerous cases, a quantity of 0.5-2.0 parts by weight for 100 parts by weight of the macromolecular elastomer polymers already gives excellent results.

Claims

1. Elastomer composition that is easy to release formed of a macromolecular elastomer and an internal release agent, characterized in that the internal release agent consists at least of an oligomer product with urethane, urea base or their mixtures fulfilling one of the following formulas:



in which A, A', B, B' and R independently of each other represent C_1-C_{35} alkyl residues or residues of substituted aryl esters, the substituents of the aryl esters being halogen atoms, C_1-C_{35} alkyl residues or C_6-C_{14} aryl, C_1-C_{15} alkylthio, C_6-C_{14} arylthio or C_7-C_{15} arylalkyl residues, A, B and R also may be hydrogen atoms, but at least one of the A, B and R residues is not hydrogen, and the X residues are oxygen or sulfur atoms, the Y and Y' residues, independently of each other, being C_1-C_{35} alkylene, C_6-C_{14} arylene, C_7-C_{30} alkylarylene, C_7-C_{20} arylalkylene, $-(CH_2)_{1-4}O-(CH_2)_{1-4}$ and $-(CH_2)_{1-4}S-(CH_2)_{1-4}$, residues or residues of polyethers, polycarbonates or polybutadiene with molecular weight from 400-4000, and a and b are whole numbers on condition that the sum a + b is at least equal to 1.

2. Composition according to Claim 1, characterized in that the oligomer products with urethane and/or urea base are present in an amount of 0.01-10.00 parts by weight for 100 parts by weight of the macromolecular elastomer mixture.

3. Composition according to Claim 1, characterized in that the oligomer products with urethane and/or urea base are present in an amount of 0.1-1.5 parts by weight for 100 parts by weight of the macromolecular elastomer mixture.

4. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is 1,6-hexanedistearyldiurethane.

5. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is 1,6-hexanedistearyldiurethane, distearylurethane or oleylstearylurethane.

6. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is the reaction product of 2 mol of stearyl alcohol and 1 mol of toluylene diisocyanate.

7. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is the reaction product of 1 mol of trimethylolpropane with 1 mol of stearylisocyanate.

8. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is the reaction product of 1 mol of trimethylolpropane with 2 mol of stearylisocyanate.

9. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is the reaction product of 1 mol of polybutadienol (with 2.3 functionality) with 2.3 mol of stearylisocyanate.

10. Composition according to any one of Claims 1-3, characterized in that the oligomer product with urethane base is the reaction product of 1 mol of glycide with 1 mol of stearylisocyanate.